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Detailed Modeling and Analysis of Aromatic Additive Effects in Ethylene-Air Flames

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Ethylene-air flames are being studied to determine the effects of small amounts of stable aromatic intermediates on the combustion chemistry as it relates to the formation of soot. We show that the introduction of aromatics into the transition regime between a well-stirred and plug flow reactor can trigger the formation of larger aromatics at various concentrations, providing information concerning the gas phase chemistry during soot inception. Gas chromatography is performed on combustion samples extracted from the plug flow reactor at known residence times for a given flame equivalence ratio and additive concentration. The additives studied include benzene and ethylbenzene. For these additives, the results show that the smaller ring compounds achieve steady state between ring formation and expansion. As residence times increase, higher molecular weight molecules are formed at higher concentrations in comparison to baseline data where no additive is introduced. This body of work provides experimental data which will be useful in the expansion of the range of conditions used to validate and “fine tune” existing PAH/Soot models.

1. Introduction

The mechanism through which soot particles are formed is complex due to multiple contributing influences such as flame structure and flow, temperature, flame composition, and equivalence ratio coupled with the multiple steps in soot formation including pyrolysis, inception, coagulation, surface growth, and ultimately particle oxidation. The details relating all of these variables and their influence on the processes involved in soot formation have yet to be resolutely defined [1]. A better understanding of the reaction chemistry and the role that additives play in the reduction of soot would provide a significant contribution in the effort to control particulate emissions.

The goal of this study is to analyze the effects of aromatic hydrocarbon additives on the gas phase chemistry of an ethylene-air flame. The fuel additives are introduced by evaporating the substance in a carrier gas and injecting the mixture as a vapor into the transition regime between the well-stirred and plug flow sections of the NIST well-stirred reactor (WSR)/plug flow reactor (PFR) experimental apparatus [2]. Gas chromatography coupled with mass spectrometry is performed on combustion samples extracted from the plug flow reactor at a known residence

time for a given flame equivalence ratio and additive concentration. The resulting chromatograms are then analyzed to determine the changes in concentration of key gas phase species. Concurrently, soot particle size distributions are measured using differential mobility analysis. Ultimately, the results of the experimental work will be leveraged, allowing for model validation for a range of conditions which will provide for more robust theoretical results and insight into how fuel additives influence soot formation.

2. Experimental Description

The unique NIST well-stirred reactor (WSR)/plug flow reactor (PFR) experimental facility was utilized in order to measure and define the reactions and changes in conditions that occur with the introduction of aromatics in fuel rich ethylene flames. The NIST WSR/PFR, depicted in Figure 1, is based on a design currently implemented by Stouffer *et al.* [3]. The reactor provides a stable and close-to-industrial scale combustor which approximates a highly turbulent combustion environment [2,4] where the turbulent time scale is much smaller (faster) than the chemistry time scale allowing for the rapid mixing of reactants and products. This turbulent mixing allows for the uniform temperature profiles that are seen in the plug flow section.

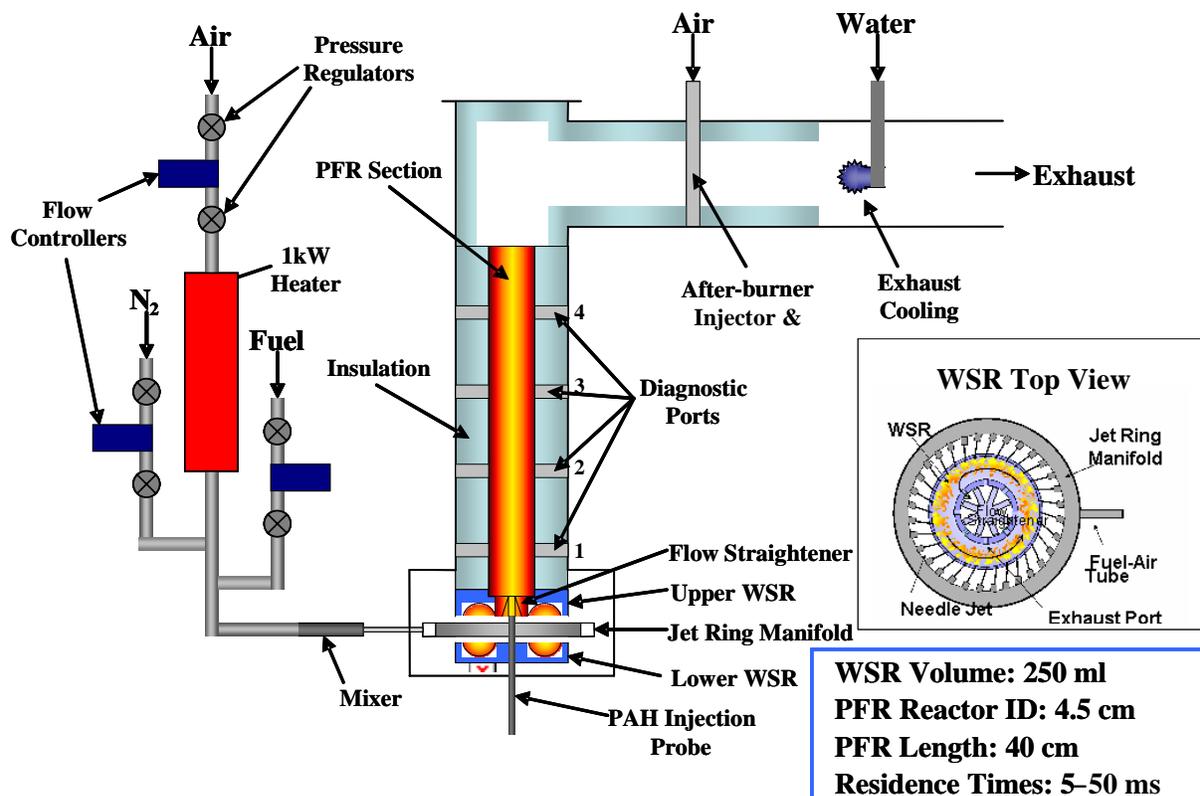


Figure 1: Schematic of the NIST WSR/PFR Experiment Apparatus

The current diagnostics interfacing with the WSR/PFR include an Agilent 6890N gas chromatograph (GC) linked to an Agilent 5975 mass spectrometer (MS), providing gas phase analysis capabilities. Temperature data are obtained with multiple thermocouples mounted on

the reactor. A diluter coupled with a nano-differential mobility analyzer (nano-DMA) which is inline with an ultrafine condensation particle counter (UCPC), described in detail by Manzello *et al.* [2,4], is in place to measure *in situ* soot particle size distribution. Further information concerning the soot particle size distribution data and related experimental methodology can be found in Manzello *et al.* [5] (another paper in these proceedings) as the specific details concerning the soot data will not be discussed in this paper. With respect to this paper, the nano-DMA/UCPC data was used simply to note the conditions at which particle formation occurred.

Aromatic additives are introduced into the WSR/PFR system through an injector probe. The details of this probe are shown in Figure 2, with its positioning shown in Figure 1. The liquid additive was introduced at varying flowrates (0.3 to 2.5 ml/min) into the heated nebulizer through the use of a peristaltic pump. Argon gas was used to drive the nebulizer, creating droplets ranging in size from 10 to 30 μm . The jet of the nebulized additive was sprayed into and vaporized in a quartz mixing chamber heated to 200 $^{\circ}\text{C}$. From there, the vaporized additive is introduced into the WSR/PFR system. Further information concerning the details of the additive system and the design of the probe used can again be found in Manzello *et al.* [5].

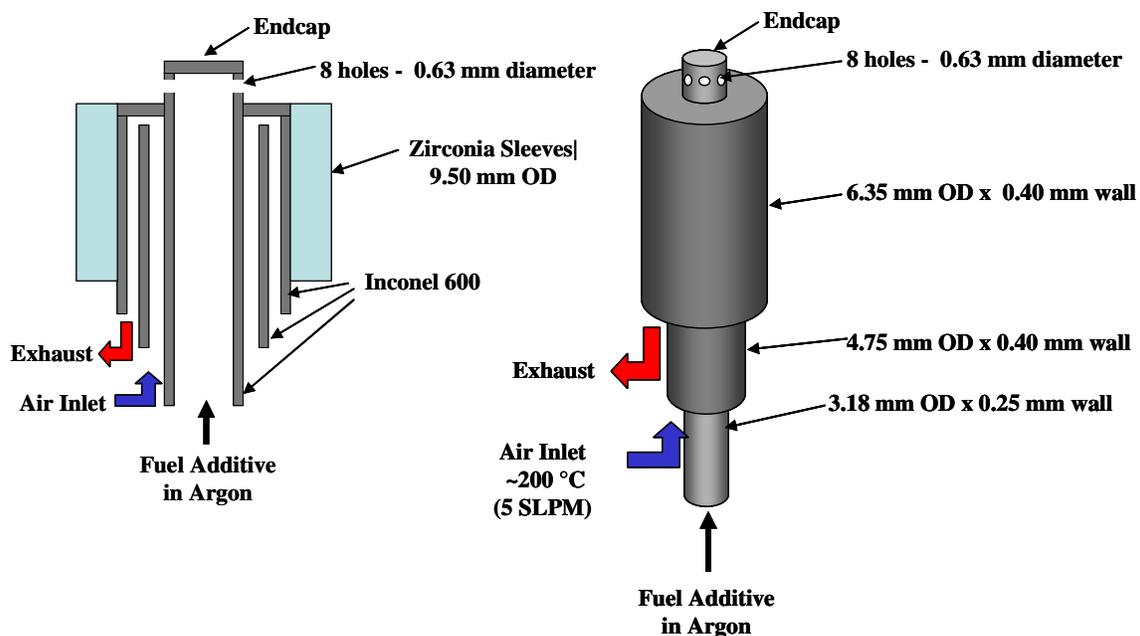


Figure 2: Schematic of Additive Injection Probe

The additive injection probe was installed in the transition regime between the WSR and the PFR, allowing the additive to participate in the combustion product reactions taking place in the PFR section. For the aromatic seeding, the flow reactor was operated under non-sooting conditions; specifically, $\Phi = 1.8$. At these operating conditions, benzene and ethylbenzene were introduced into the system to study the subsequent additive effects on the gas phase species concentration and soot size distributions [5]. In all cases, the controlled introduction of the aromatic additive induced the formation of soot particles.

GC/MS analysis, using a 30 m x 0.32 mm ID Agilent J&W DB-1 column with a 3 μm film thickness, was performed on combustion samples extracted from the well-stirred and plug flow sections of the reactor for a given equivalence ratio and known residence time. Figure 1 shows the four diagnostic ports that were used, numbered 1 to 4, with a residence time increase of ~ 15 ms between ports. Each effluent gas sample was introduced onto the GC column for separation and then the sample stream was split and directed to both the MS and GC flame-ionization detector (FID) for simultaneous analysis. The MS was used to identify and the FID was used to quantify all individual species. Gas standards of known concentrations were used to calibrate the system and to calculate the GC FID response factors used to quantify the species based on an effective carbon-atom number basis [6,7]. Where calibration standards were not available, heptane was the reference material used for quantification of the lighter hydrocarbon species (up to C_5). Benzene was used as the reference material for the aromatic hydrocarbon species (C_6 and larger).

When sampling hot combustion gas, there is the need to quench the sample to capture the species concentrations at the point of extraction, but there is also a concern with cooling the sample gases to the point that certain species are condensed out. To mitigate this problem, an oil cooled probe was designed, shown in Figure 3, which quenched and maintained the sample gases at a temperature of 150°C , addressing both concerns. Three concentric stainless steel (SS) tubes were used to create a coolant circulation path, cooling the sample gases in the centermost SS $1/8''$ OD tube to 150°C . This inner $1/8''$ OD tube was secured by an inconel cap welded to the outer SS $3/8''$ OD tube. The coolant was maintained at temperature by a recirculating heated bath. The oil cooled design allowed for an order of magnitude improvement in the quench times in comparison to those measured with a non-temperature controlled ceramic sampling probe. With the oil cooled probe, the gases were maintained at 150°C throughout the sampling system up to the point of introduction into the GC. A valving system consisting of twelve 1 ml sample loops was employed to aid in sample storage and processing efficiency, enabling the analysis of multiple samples at varying conditions during a single reactor run. The GC analysis temperature profile ranged from -60°C up to 280°C , allowing for the quantification of light hydrocarbons and heavier polycyclic aromatic hydrocarbons (PAHs) with a single effluent gas sample.

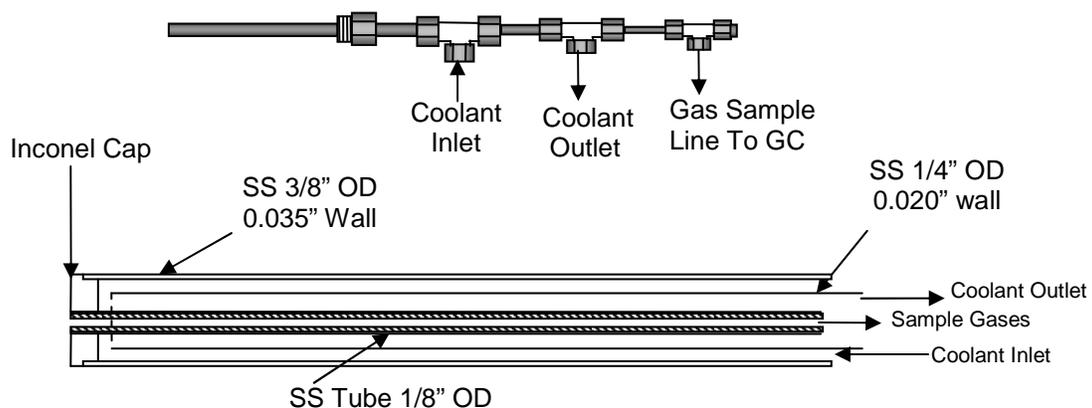


Figure 3: Schematic of oil cooled gas sampling probe

3. Results and Discussion

Figure 4 shows the change in gas phase species concentration with increase in residence time with the addition of 725 ppm (0.66 ml/min) of benzene for a representative range of combustion products found in the PFR effluent gases. The introduction of benzene increases the global

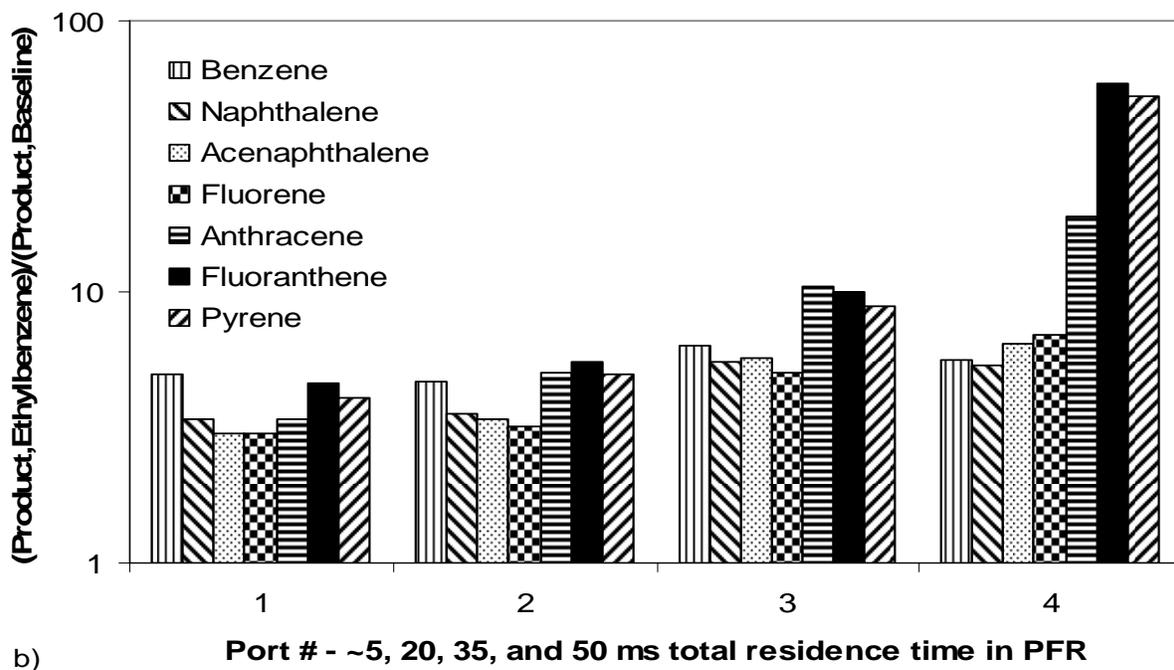
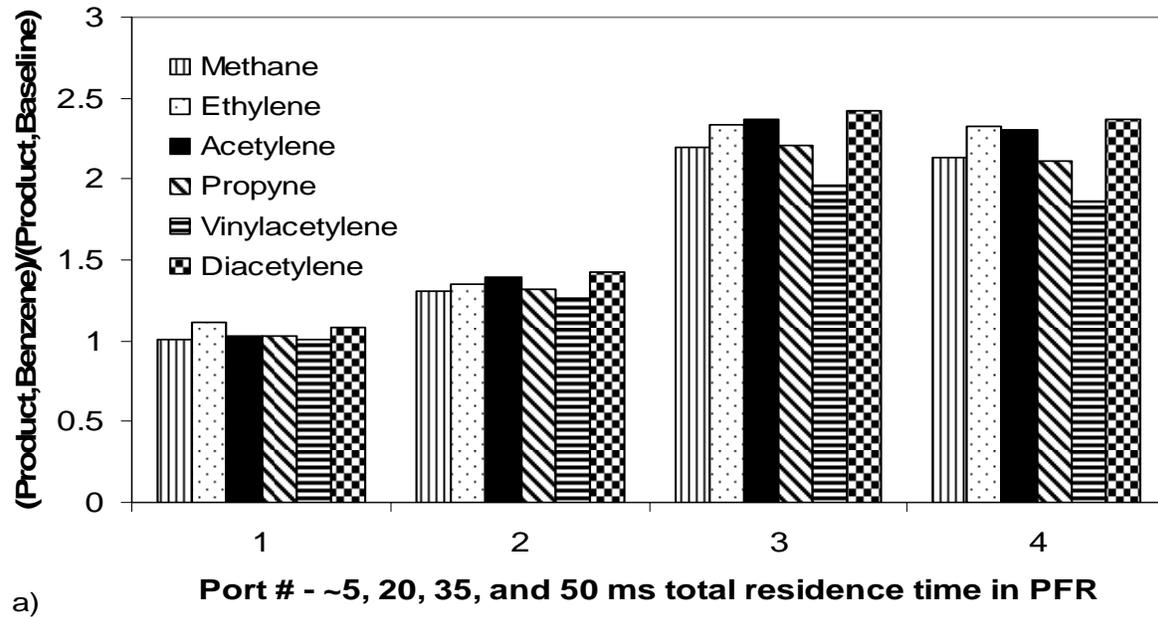


Figure 4: Comparison of changes in gas phase species concentration as a function of increasing residence time with the addition of 725 ppm of benzene at ~1300 K and 1 bar.
 a) lighter hydrocarbons (less than C₆) b) heavier hydrocarbons (C₆ or greater)

equivalence ratio to approximately 1.82 which is still a non-sooting condition for the ethylene-air flame. If the ethylene flow rate was increased into the WSR to these equivalence ratios, no particle formation is observed. The additive data are normalized relative to the baseline data of $\Phi = 1.8$ with no additive. Table 1 provides the measured gas phase species concentrations (ppm) at these conditions. The results from benzene addition are illustrative of the continual formation of ring structures. For the smaller ring compounds there appears to be an achievement of a steady state between ring formation and expansion. As residence times increase, higher molecular weight molecules are being formed at higher concentrations. Particularly impressive is the precipitant increase of the fluoranthene and pyrene structures between the 3rd and 4th ports. From a mass balance consideration it would appear that a significant quantity of the benzene is being recovered in the larger ring compounds. All of these point to benzene or phenyl as the precursor. This is of course highly speculative. We are carrying out detailed modeling studies to place these observations on a more quantitative basis.

Table 1: $\Phi = 1.8$, 725 ppm Benzene Additive

Species Name	Port 1 Concentration (ppm)	Port 2 Concentration (ppm)	Port 3 Concentration (ppm)	Port 4 Concentration (ppm)
Methane	5000	5157	5127	5179
Ethylene	172	168	172	188
Acetylene	14227	14106	13525	13189
Vinylacetylene	45	41	39	38
Diacetylene	551	520	482	462
Benzene	287	265	250	260
Naphthalene	43	50	56	63
Acenaphthalene	50	71	87	99
Fluorene	2.6	3.0	2.8	3.0
Anthracene	4.1	7.1	9.0	16
Fluoranthene	1.7	3.3	5.0	26
Pyrene	2.4	5.0	7.6	40

Ethylbenzene was another liquid aromatic that was introduced into the reactor at a flowrate of 0.66 ml/min (526 ppm) and an ethylene-air equivalence ratio of 1.8. Once again the aromatic seeding triggered the formation of soot particles under typically non-sooting conditions. The results, normalized relative to the baseline data of $\Phi = 1.8$ with no additive, are presented in Figure 5 along with the tabulated data in Table 2.

It is clear that ethylbenzene and particularly its breakdown products are less able to participate in the processes that lead to large-ring formation. On the other hand, for benzene we are clearly in the kinetic region where benzene and/or its decomposition products are actively contributing to larger ring formation. The most likely breakdown product from ethylbenzene is the benzyl radical. It would appear that under the present conditions of 1300 K, 1 bar pressure and residence times increasing from 5 to 50 ms, the condensation products of benzyl and other reactive radicals do not contribute to the significant formation of larger aromatic rings. Furthermore, the breakdown of benzyl leads to concentrations of benzene or its breakdown

products that are much smaller in comparison to those formed when benzene is directly introduced. This has implications on the mechanism for benzyl radical decomposition.

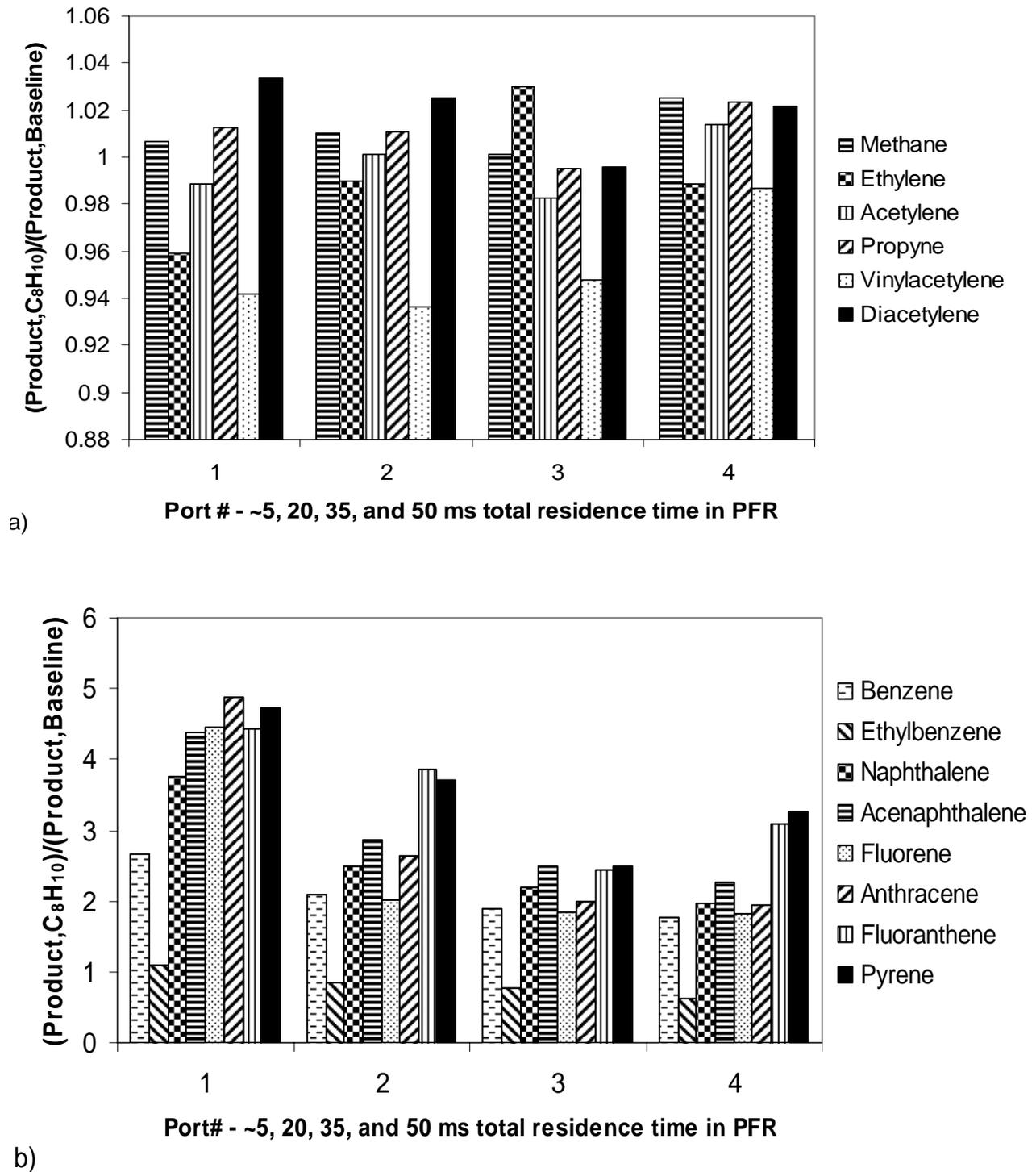


Figure 5: Comparison of changes in gas phase species concentration as a function of increasing residence time with the addition of 526 ppm of ethylbenzene at ~ 1300 K and 1 bar. a) lighter hydrocarbons (less than C_6) b) heavier hydrocarbons (C_6 or greater)

Table 2: $\Phi = 1.8$, 526 ppm Ethylbenzene Additive

Species Name	Port 1 Concentration (ppm)	Port 2 Concentration (ppm)	Port 3 Concentration (ppm)	Port 4 Concentration (ppm)
Methane	4253	4473	4579	4684
Ethylene	104	108	118	122
Acetylene	10147	10006	13525	13189
Vinylacetylene	29	27	26	26
Diacetylene	384	360	348	323
Benzene	92	93	97	99
Ethylbenzene	<1	<1	<1	<1
Naphthalene	21	21	22	22
Acenaphthalene	29	34	38	38
Fluorene	1.1	0.85	0.84	0.82
Anthracene	2.9	2.9	3.4	3.5
Fluoranthene	1.7	1.5	1.9	2.4
Pyrene	2.4	2.4	3.0	3.9

4. Conclusions

A gas chromatograph inline with a mass spectrometer was used to identify and quantify the gas phase species found in the WSR/PFR effluent stream, measuring the effects of small amounts of stable aromatic intermediates on the combustion chemistry as it relates to the formation of soot. The results clearly demonstrate that the described method of aromatic additive introduction can seed the combustion process, triggering the formation of soot in a highly controlled manner. We show that the introduction of the aromatics can trigger the formation of larger aromatics at various concentrations, providing information concerning the gas phase chemistry during soot inception. Through the systematic introduction of possible precursors it should be possible to narrow the range of possible reactions and at the same time determine quantitative values for the rate constants of the important reactions. The experimental data described are being used to develop and validate a quantitative kinetic database for PAH growth and a soot inception model.

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References

- [1] H. Richter and J.B. Howard, *Prog. Eng. Combust. Sci.* 26: 565-608 (2000).
- [2] S.L. Manzello, D.B. Lenhart, A. Yozgatligil, M.T. Donovan, G.W. Mulholland, M.R. Zachariah, and W. Tsang, *Proc. Combust. Inst.* 31: 675-683 (2007).
- [3] Stouffer, S.D., Striebich, R.C., Frayne, C.W., and Zelina, J., *38th Joint Propulsion Conference & Exhibit*, July 7-10, Indianapolis, Indiana (2002).

- [4] Manzello, S.L., Mulholland, G.W., Donovan, M.T., Tsang, W., *4th Joint Meeting of the US Sections of the Combustion Institute*, March 20-23, Philadelphia, PA (2005).
- [5] S.L. Manzello, D. B. Lenhert, C.B. Stroud, and W. Tsang, "The Effects of Aromatic Species on Soot Particle Size Distributions in a Well-Stirred Reactor/Plug Flow Reactor," 5th Joint Meeting of the US section of the Combustion Institute, 25-28 March 2007, San Diego, CA.
- [6] Scanlon, J.T. and Willis, D.E., *Journal of Chromatographic Science*, 23: 333-340 (1985).
- [7] Kallai, M. and Balla, J., *Chromotographia*, 56: 357-360 (2002).